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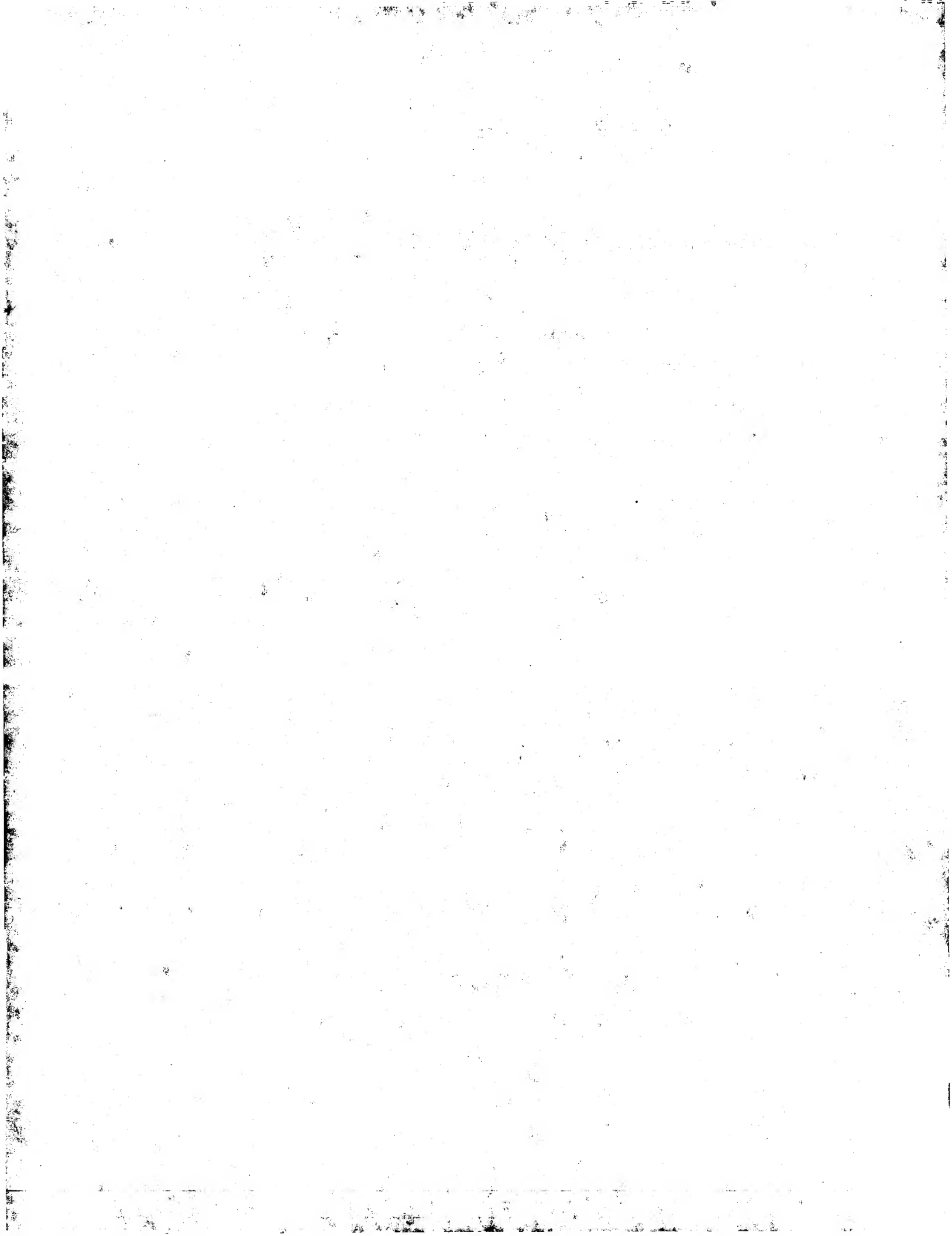
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# PATENT SPECIFICATION

NO DRAWINGS

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L082,945

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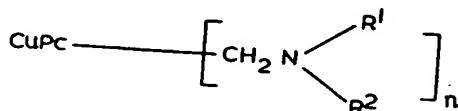
## COMPLETE SPECIFICATION Manufacture of Pigment Compositions

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1., a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention, which is a modification of the invention claimed in United Kingdom Application No. 9804/62 (Serial No. 972805) relates to pigment compositions having improved resistance to flocculation and to the manufacture of such pigment compositions.

United Kingdom Application No. 9804/62 (Serial No. 972,805) claims a pigment composition comprising a pigment intimately incorporated with a minor quantity of an organic pigment derivative containing a secondary or tertiary amino group, the nitrogen atom of said group being attached to the remainder of the molecule through a methylene group.

A preferred pigment composition claimed in the said application comprises a copper phthalocyanine or copper monochlorophthalocyanine intimately incorporated with a copper phthalocyanine derivative of the formula

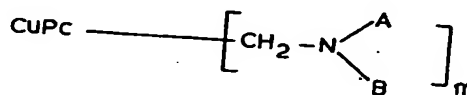


wherein CuPc represents copper phthalocyanine, R<sup>1</sup> represents hydrogen or an alkyl or hydroxyalkyl radical, R<sup>2</sup> represents an alkyl, cycloalkyl, hydroxyalkyl, aminoalkyl or aralkyl radical and n is an integer from 1 to 5.

The pigment compositions of United Kingdom Application No. 9804/62 (Serial No. 972,805) are valuable because of their

high resistance to flocculation and crystal growth in non-aqueous media. We have now found that similar advantageous properties are possessed by a pigment composition in which a more highly substituted copper phthalocyanine derivative is incorporated.

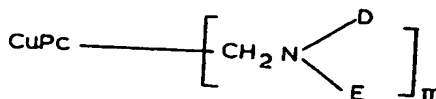
According to the invention we provide a pigment composition comprising copper phthalocyanine or copper monochlorophthalocyanine intimately incorporated with a copper phthalocyanine derivative of the formula



formula 1.

wherein CuPc represents copper phthalocyanine, A represents hydrogen or an alkyl or hydroxyalkyl radical, B represents an alkyl, cycloalkyl, hydroxyalkyl, aminoalkyl or aralkyl radical, or A and B may be linked together and jointly represent the atoms necessary to complete a heterocycle containing the nitrogen atom, and m is an integer from 6 to 8.

A preferred pigment composition of our invention comprises copper phthalocyanine or copper monochlorophthalocyanine intimately incorporated with a copper phthalocyanine derivative of the formula



formula 2.

wherein CuPc represents copper phthalocyanine, D represents hydrogen or a hydroxy-

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alkyl radical of 2 to 4 carbon atoms, E represents an alkyl radical of 1 to 22 carbon atoms and m is an integer from 6 to 8.

According to a further feature of the invention we manufacture a pigment composition by intimately incorporating copper phthalocyanine or copper monochlorophthalocyanine with a copper phthalocyanine derivative of formula 1 or formula 2.

Incorporation of the pigment with the pigment derivative may be carried out in various ways, for example during acid pasting or salt milling of the pigment. Such techniques for incorporating pigment derivatives are described in United Kingdom Application No. 9804/62 (Serial No. 972,805).

An excellent method for manufacturing the pigment compositions of our invention comprises milling an aqueous suspension of the copper phthalocyanine or copper monochlorophthalocyanine and the copper phthalocyanine derivative in the presence of a grinding aid, preferably a particulate grinding aid such as sand or beads of porcelain, glass or insoluble plastic material. If desired, such milling may be carried out in presence of an acid and the pH may subsequently be raised to liberate the free base form of the derivative.

Pigment derivatives for use in the manufacture of the pigment compositions of our invention may be obtained by reacting the appropriate amines and copper chloromethyl phthalocyanines. Mixtures of copper hexahepta- and octa-chloromethyl phthalocyanines may be employed. It is not harmful for the copper chloromethylphthalocyanine to contain a proportion of less highly chloromethylated analogues.

Amines which may be reacted with such chloromethyl compounds include methylamine, ethylamine, isopropylamine, octylamine, dodecylamine, cetylamine, ethanollamine, cyclohexylamine, benzylamine, morpholine, piperidine, hexamethyleneimine and 2-ethylaminoethanol.

The proportions of pigment and organic pigment derivative in the pigment composition of the invention are not critical. We find that pigment compositions containing from 1 to 20%, and especially from 2% to 10% by weight of the organic pigment derivative have excellent properties.

The pigment compositions of our invention, especially those of the preferred type are of value as colouring matters for paints, lacquers, enamels, printing inks, plastic materials and the like because they disperse rapidly in non-aqueous media and have a high degree of resistance to flocculation and to crystal growth.

The invention is illustrated but not limited by the following Examples in which all parts and percentages are by weight.

#### EXAMPLE 1

26 parts of cyclohexylamine are stirred

whilst 4 parts of copper octa-(chloromethyl)-phthalocyanine are added. After stirring at 90° to 100°C. for 16 hours the mixture is cooled and diluted with 100 parts of water. The solid copper octa(cyclohexylaminomethyl)phthalocyanine is filtered off, washed with water and dried.

20 parts of copper phthalocyanine (as obtained by the reaction of phthalic anhydride, urea, copper chloride and a catalyst in an inert solvent), 1 part of copper octa(cyclohexylaminomethyl)phthalocyanine, 5 parts of 80% phosphoric acid and 97 parts of water are charged into a stainless steel beaker which is fitted with a stirrer and contains 360 parts of sand (of particle size 0.25—0.3 mm). The stirrer is driven at 1680 revolutions per minute for 3 hours. The sand is then removed by sieving through a cloth and the suspension is neutralised with 2N sodium hydroxide solution. The solid matter is then filtered, washed with water until electrolytes are removed, and dried at 100°C.

The pigment composition so obtained is readily dispersed in paint media by conventional methods. In air drying alkyd paint media it shows exceptionally high resistance to flocculation.

#### EXAMPLE 2

69.4 parts of isopropylamine are stirred whilst 20 parts of copper octa-(chloromethyl)-phthalocyanine are added. After stirring at the boiling point for 16 hours and then diluting with water, the solid copper octa(isopropylaminomethyl)phthalocyanine is filtered off, washed and dried. It is soluble in 6% acetic acid.

A mixture of 30 g. of crude copper phthalocyanine, 1.5 g. of copper octa(isopropylaminomethyl)phthalocyanine, 1.5 g. of 80% phosphoric acid and 87 g. of water is milled with 360 g. of no. 10 beads for 3 hours in a stainless steel beaker fitted with a stainless steel rotor with 2½" diameter discs rotating at 1680 r.p.m. After diluting with 100 parts of water and separating from the beads by filtering through cloth, the suspension is made alkaline by addition of 8% sodium hydroxide solution. The pigment is filtered off, washed and dried. The resulting pigment exhibits excellent tinctorial strength on milling into lithographic varnish to give a printing ink.

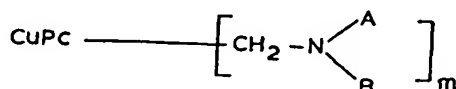
#### EXAMPLE 3

26.5 parts of benzylamine are stirred whilst 4 parts of copper octa-(chloromethyl)phthalocyanine are added. After stirring at 90° to 100° for 16 hours, cooling and diluting with methanol, the solid copper octa(benzylaminomethyl)phthalocyanine is filtered off, washed with methanol and dried.

When used instead of copper octa(cyclohexylaminomethyl)phthalocyanine in the procedure described in Example 1 it affords a similar pigment composition.

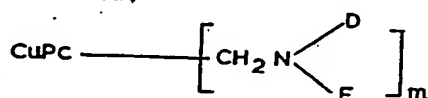
## WHAT WE CLAIM IS:—

1. A pigment composition comprising copper phthalocyanine or copper monochlorophthalocyanine intimately incorporated with a copper phthalocyanine derivative of the formula



wherein CuPC represents copper phthalocyanine, A represents hydrogen or an alkyl or hydroxyalkyl radical, B represents an alkyl, cycloalkyl, hydroxyalkyl, aminoalkyl or aralkyl radical, or A and B may be linked together and jointly represent the atoms necessary to complete a heterocycle containing the nitrogen atom, and m is an integer from 6 to 8.

2. A pigment composition comprising copper phthalocyanine or copper monochlorophthalocyanine intimately incorporated with a copper phthalocyanine derivative of the formula



wherein CuPC represents copper phthalocyanine, D represents hydrogen or a hydroxyalkyl radical of 2 to 4 carbon atoms, E represents an alkyl radical of 1 to 22 carbon atoms and m is an integer from 6 to 8.

3. A pigment composition according to claim 1 or 2 wherein the percentage by weight of copper phthalocyanine derivative is from 1% to 20%.

4. A pigment composition according to claim 1 or 2 wherein the percentage by weight of copper phthalocyanine derivative is from 2% to 10%.

5. A pigment composition according to any of the preceding claims wherein the phthalocyanine derivative is a mixture of phthalocyanine derivatives in which m is 6, 7 and 8.

6. A process for the manufacture of a pigment composition as claimed in any one of claims 1 to 5 which comprises intimately incorporating copper phthalocyanine or copper monochlorophthalocyanine with a copper phthalocyanine derivative of formula 1 or formula 2.

7. Process for the manufacture of a pigment composition according to claim 6 which comprises acid pasting the copper phthalocyanine or copper monochlorophthalocyanine with the copper phthalocyanine derivative.

8. Process for the manufacture of a pigment composition according to claim 6 which comprises salt milling the copper phthalocyanine or copper monochlorophthalocyanine with the copper phthalocyanine derivative.

9. Process for the manufacture of a pigment composition according to claim 6 which comprises milling an aqueous suspension of the copper phthalocyanine or copper monochlorophthalocyanine and the copper phthalocyanine derivative in presence of a particulate grinding aid.

10. Process according to claim 9 wherein the milling is carried out in presence of acid and the pH subsequently raised to liberate the free base form of the copper phthalocyanine derivative.

11. A pigment composition substantially as hereinbefore particularly described especially with reference to the foregoing Examples.

12. Process for the manufacture of a pigment composition substantially as hereinbefore particularly described especially with reference to the foregoing Examples.

13. Process for the manufacture of a dispersion of a pigment composition in a paint or printing ink medium which comprises incorporating into said medium a pigment composition as claimed in any of claims 1 to 5 and 11.

14. Paints, lacquers, enamels, printing inks and plastic materials containing a pigment composition according to any of Claims 1 to 5 and 11.

WALTER SCOTT,  
Agent for the Applicants.

